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Ester Interchange Reaction Catalyzed by Lanthanoid Tri-2-propoxides

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Synopsis. Lanthanoid tri-2-propoxides ($[Ln(OPr^i)_3]_n$ Ln=La, Nd, Gd, Yb) are active catalysts for the interchange reaction of the alkoxyl groups between two kinds of esters. The La catalyst is the most active among them, and the activity is higher in nonpolar solvents than in polar ones. The La catalyst is applicable to the ring-opening polymerization of 6-hexanolide.

Although much attention has been focused on the application of lanthanoid compounds in organic synthesis during the last decade,[1] only a few reactions using lanthanoid alkoxides have been reported.[2,3] The alkoxides are typical complexes of hard lanthanoid elements, and their preparation methods were established several decades ago.[4] One of the well known methods is *trans*-alkoxylation of lanthanoid tri-2-propoxides with various acetates to give the corresponding alkoxides.[5] However, this *trans*-alkoxylation has not been applied to any organic syntheses to date. Therefore, we investigated the catalytic ester interchange reactions using lanthanoid tri-2-propoxides.

An interchange reaction between methyl benzoate and ethyl butyrate rapidly proceeded at 10 °C in the presence of $La(OPr^i)_3$[6] in benzene, and attained equilibrium after about 3 h. After being further stirred at 10 °C, however,

$$\mathrm{PhCOOMe} + \mathrm{CH_3CH_2CH_2COOEt} \xrightleftharpoons[\text{10 °C in benzene}]{[\mathrm{La(OPr}^i)_3]_n} \mathrm{PhCOOEt} + \mathrm{CH_3CH_2CH_2COOMe} \tag{1}$$

the clear reaction mixture gradually changed to a white suspension. The white precipitate which was separated from the suspension contained lanthanum, but did not show the catalytic activity for the interchange reaction (Fig. 1). On acidolysis with dilute hydrochloric acid, the precipitate liberated methanol, ethanol and 2-propanol in the ratio of about 10 : 3 : 1, which was determined by gas chromatography. These results suggest that the catalytically active species are $[La(OPr^i)_m(OR)_{3-m}]_n$ (m=1, 2 and R=Me, Et) which are soluble in toluene, and that the precipitates are mostly fully substituted alkoxides, $La(OR^i)_3$ (R=Me, Et), which are catalytically inactive because of their insolubility in organic solvents.[5,8] Therefore, the subsequent reactions were carried out at 0 °C so as not to form the precipitates.

The solvent effect was investigated in terms of the yield of ethyl benzoate at nonequilibrated stages in the interchange reaction of methyl benzoate with ethyl acetate using $[La(OPr^i)_3]_n$ as the catalyst (Table 1). The yield was the highest in toluene and decreased in the following order; $CHCl_3 > CH_2Cl_2 >$ THF. The order seems to be related to the polarity of the solvents. When methyl and ethyl acetates themselves were used as the solvents, the ester interchange reactions could not be carried out, because the white precipitates were formed immediately on addition of the solvents to the catalyst. This fact indicates that the fully substitution of $[La(OPr^i)_3]_n$ to the insoluble methoxide or ethoxide is very fast at high concentrations of methyl or ethyl acetates even at low temperatures.

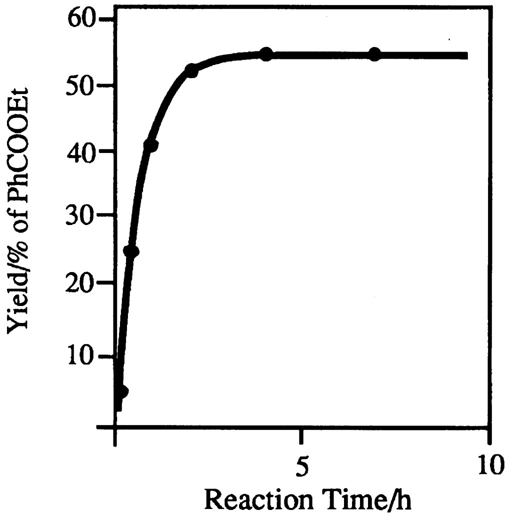


Fig. 1. Ester interchange reaction of methyl benzoate and ethyl butyrate. The reaction was carried out using PhCOOMe (5 mmol), n-PrCOOEt (5 mmol), $La(OPr^i)_3$ (0.1 mmol), and toluene (5 cm^3) at 10 °C.

Table 1. Solvent Effect on Alkoxyl Interchange Reaction of Methyl Benzoate with Ethyl Acetate

Solvent	Yield/% of PhCOOEt
Toluene	57
Chloroform	54
Dichloromethane	39
Tetrahydrofuran	32

The reactions were carried out using $La(OPr^i)_3$ (0.1 mmol), PhCOOMe (1.0 mmol), MeCOOEt (10 mmol) and solvent (5 cm^3) at 0 °C for 2 h. The yields were determined by GLC.

Table 2. Catalytic Activity of Lanthanoid Tri-2-propoxides

Catalyst	Yield/% of PhCOOEt
$[\mathrm{La(OPr}^i)_3]_n$	57
$[\mathrm{Nd(OPr}^i)_3]_n$	21
$[\mathrm{Gd(OPr}^i)_3]_n$	18
$[\mathrm{Yb(OPr}^i)_3]_n$	5

The reaction conditions are the same as in Table 1.

$$[\mathrm{La(OPr}^i)_3]_n \xrightarrow[-\mathrm{AcOPr}^i]{\mathrm{AcOR}} [\mathrm{La(OPr}^i)_2(\mathrm{OR})]_n$$

$$\xrightarrow[-\mathrm{AcOPr}^i]{\mathrm{AcOR}} [\mathrm{La(OPr}^i)(\mathrm{OR})_2]_n \qquad (2)$$

$$\xrightarrow[-\mathrm{AcOPr}^i]{\mathrm{AcOR}} [\mathrm{La(OR)}_3]_n$$

$$\mathrm{R} = \mathrm{Me, Et}$$

The catalytic activity of various lanthanoid tri-2-propoxides was examined in the same way as above using toluene as the solvent. The catalytic activity increased in the order La>Nd>Gd>Yb, which clearly corresponds with the order of metal ion size (Table 2). An analogous dependency on metal size has been observed in other Ln-catalyzed reactions.[3,9,10] An increase in the metal ion size is considered to lead to the increases in basicity as well as in the coordinative unsaturation of the alkoxides. The former effect has been proposed in the Michael addition and aldol reactions catalyzed by lanthanoid trialkoxides,[3] and the latter steric factor has been claimed in the hydroamination with $(\mathrm{Me_5C_5})_2\mathrm{LnCH(TMS)_2}$.[10] However, in this ester interchange reaction, the increasing basicity of the catalysts is presumably more important for enhancing the catalytic activity, because the ester interchange reaction is substantially catalyzed by bases or acids.

The reactivity of substrates was examined in the interchange reaction of different methyl esters (5 mmol) with ethyl acetate (5 mmol) in the presence of

$$R\text{-COOMe} \xrightarrow[{[\mathrm{La(OPr}^i)_3]_n \text{ in Toluene at } 0\ ^\circ\mathrm{C}}]{\mathrm{AcOEt}} R\text{-COOEt} \qquad (3)$$

R (Relative Rate)
Ph (100) > n-Pr (88) > i-Pr (34) > t-Bu (18)

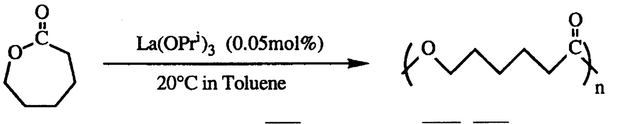
$\mathrm{La(OPr}^i)_3$ (0.1 mmol) in toluene (5 cm^3) at 0 °C. In the case of methyl benzoate (R=Ph), the initial formation rate of ethyl benzoate was 71 μmol min^{-1}. Compared with this aromatic carboxylic acid ester, every tested alkanoate exhibited low reactivities. Except for methyl benzoate, the reactivity of alkanoates seems to depend on the steric factor of the substituents on the carbonyl carbon.

The effect of alkoxyl substituents was investigated in the alkoxyl interchange reaction of several acetates with methyl benzoate under the same conditions as above. The effect of the substituents at the oxygen atom was markedly greater than that at the carbonyl carbon, even though the electronic influence on the carbonyl group, which is the reaction center, is more sensitive to substituents at the carbonyl carbon than at the oxygen atom. The interchange reaction of phenoxyl group was much slower than the ethoxyl interchange, even though the phenoxyl group is more electron-withdrawing than the latter group. These facts indicate that the ester interchange reaction is mainly governed by the steric factor of substrates rather than the electronic factor.

$$\text{PhCOO-Me} \xrightarrow[{[\mathrm{La(OPr}^i)_3]_n \text{ in Toluene at } 0\ ^\circ\mathrm{C}}]{\text{AcO-}R} \text{PhCOO-}R \qquad (4)$$

R (Relative Rate)
Et (100) > i-Pr (1.3) > Ph (1) > t-Bu (0.4)

This ester interchange reaction, which involves the scission of carbonyl–alkoxy bond, was applicable to the ring-opening polymerization of 6-hexanolide. The lactone polymerization, which has attracted current interest because of the high biodegradability of the polymer, has been reported mostly by use of aluminum alkoxides.[11,12] The polymerization of 6-hexanolide was very fast in the presence of $\mathrm{La(OPr}^i)_3$, and the mixture rapidly became viscous without depositing precipitate. The polymer whose melting point was about 60 °C was obtained as a white solid in a 50% yield. In spite of this low yield, the polymer showed rather high $\overline{M_\mathrm{n}}$ and narrow $\overline{M_\mathrm{w}}/\overline{M_\mathrm{n}}$ values which were determined by GPC. This fact presumable indicates that every 2-propoxyl group is not able to contribute to the initiation of polymerization because of the polymeric nature of lanthanum tri-2-propoxide.[13]



$$\overline{M_\mathrm{n}} = 58000, \quad \overline{M_\mathrm{w}}/\overline{M_\mathrm{n}} = 1.4 \qquad (5)$$

Experimental

General Comments. All reactions were carried out with the use of standard Schlenk procedures under an argon atmosphere. Toluene, benzene and THF were distilled under argon from sodium benzophenone ketyl. Chloroform and dichloromethane were refluxed over calcium hydride and distilled. All esters were dried over calcium hydride and purified by distillation perior to use. Lanthanoid tri-2-propoxides were prepared according tò previously described method.[16]

Gas chromatographic analyses were performed using a Yanagimoto G-2800 with a flame ionization detector. Analytical gel permeation chromatography was carried out using a Shimadzu RID-6A equipped with an Asahipack GS-510 column. The column was calibrated with polystyene standards using THF as solvent at 25 °C.

Catalytic Ester Interchange Reaction. A typical experiment was carried out as follows. A solution of $Ln(OPr^i)_3$ (0.1 mmol) and naphthalene or durene as an internal calibration standard in a solvent (5 cm^3) was cooled to 0 °C in an ice bath. A mixture of methyl ester and another ester was added, and the reaction mixture was stirred and maintained at 0 °C. The reaction was monitored with GLC, for which samples were withdrawn periodically with a syringe and immediately quenched with an aqueous sodium chloride solution containing a small amount of hydrochloric acid.

Polymerization of 6-Hexanolide. To a stirred solution of $La(OPr^i)_3$ (16 mg, 0.05 mmol) in toluene (100 cm^3) at 20 °C was added dropwise 6-hexanolide (23 g, 0.2 mol). The mixture was stirred for 3 h, during which time the solution became very viscous. The polymerization was quenched with a mixture of saturated aqueous sodium chloride (20 cm^3) and concentrated hydrochloric acid (1 cm^3). The organic layer was washed with water and dried over anhydrous sodium sulfate. After filteration, the toluene solution was dropped into cold pentane (500 cm^3, 0 °C) to form white solids. The cold solution was decanted off, and the polymer was washed with pentane and dried in vacuo at 40 °C, 11.2 g (50%), mp 60 °C.

References

1) W. J. Evans, *Adv. Organomet. Chem.*, **24**, 131 (1985); P. L. Watson and G. W. Parshall, *Acc. Chem. Res.*, **18**, 51 (1985); B. E. Kahn and R. D. Rieke, *Chem. Rev.*, **88**, 733 (1988); G. A. Molander, *Chem. Rev.*, **92**, 29 (1992), and references cited therein.

2) K. S. Kirshenbaum, *Nouv. J. Chim.*, **7**, 699 (1983); J. -L. Namy, J. Souppe, J. Collin, and H. B. Kagan, *J. Org. Chem.*, **49**, 2045 (1984); K. Yokoo, N. Mine, H. Taniguchi, and Y. Fujiwara, *J. Organomet. Chem.*, **279**, C19 (1985); J. Prandi, J. -L. Namy, G. Menoret, and H. B. Kagan, *J. Organomet. Chem.*, **285**, 449 (1985); J. Collin, J. -L. Namy, and H. B. Kagan, *Nouv. J. Chim.*, **10**, 229 (1986); T. Okano, M. Matsuoka, H. Konishi, and J. Kiji, *Chem. Lett.*, **1987**, 181; D. A. Evans and A. H. Hoveyda, *J. Am. Chem. Soc.*, **112**, 6477 (1990); A. Lebrun, J. -L. Namy, and H. B. Kagan, *Tetrahedron Lett.*, **32**, 2355 (1991).

3) T. Okano, K. Ohono, and J. Kiji, *Chem. Express*, **7**, 393 (1992); H. Sasai, T. Suzuki, S. Arai, T. Arai, and M. Shibasaki, *J. Am. Chem. Soc.*, **114**, 4418 (1992).

4) H. Adkins and F. W. Cox, *J. Am. Chem. Soc.*, **60**, 1151 (1938); R. C. Mehrotra, P. N. Kapoor, and J. M. Batwara, *Coord. Chem. Rev.*, **31**, 67 (1980); K. C. Malhotra and R. L. Martin, *J. Organomet. Chem.*, **239**, 159 (1892), and references cited therein.

5) B. S. Sankhla and R. N. Kapoor, *Aust. J. Chem.*, **20**, 2013 (1967); P. P. Sharma and R. C. Mehrotra, *J. Indian Chem. Soc.*, **45**, 736 (1968); R. C. Mehrotra and J. M. Batwara, *Inorg. Chem.*, **9**, 2505 (1970).

6) The lanthanoid triisopropoxides were prepared from metal shavings and isopropanol because the alkoxides prepared from LnX_3 and alkali metal alkoxides have sometimes been reported to contain chlorine or alkali metals.[7]

7) R. A. Andersen, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, **17**, 1962 (1978); W. J. Evans, M. S. Sollverger, and T. P. Hanusa, *J. Am. Chem. Soc.*, **110**, 1841 (1988), and references cited therein.

8) J. A. Batwara, U. D. Tripathi, and R. C. Mehrotra, *J. Chem. Soc. A*, **1967**, 991; A. Mehrotra and R. C. Mehrotra, *Indian J. Chem.*, **10**, 532 (1972).

9) G. Jeske, H. Lauke, H. Mauermann, P. N. Swepston, H. Schumann, and T. J. Marks, *J. Am. Chem. Soc.*, **107**, 8091 (1985); G. Jeske, H. Lauke, H. Mauermann, H. Schumann, and T. J. Marks, *J. Am. Chem. Soc.*, **107**, 8111 (1985).

10) M. R. Gagné, C. L. Stern, and T. J. Marks, *J. Am. Chem. Soc.*, **114**, 275 (1992).

11) T. Ouhadi, C. Stevens, and P. Teyssie, *Makromol. Chem. Suppl. 1*, **1975**, 191; A. Hofman, S. Slomkowski, and S. Penczek, *Makromol. Chem. Rapid Commun.*, **8**, 387 (1987); M. Endo, T. Aida, and S. Inoue, *Makromolecules*, **20**, 2982 (1987).

12) Recently, the ring-opening polymerization catalyzed by lathanoid complexes was reported: S. J. McLain, T. M. Ford, and N. E. Drysdale, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **33**, 443 (1992); S. J. MacLain and N. E. Drysdale, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **33**, 174 (1992).

13) Their polymeric nature is unquestionable[3,4,7] though little information has been known about the definite structure of lanthanoid alkoxides except for $Ce_2(OCBu^t_3)_4(OBu^t)_2$[14] and $Y_5O(OPr^i)_{13}$.[15]

14) A. Sen, H. A. Stecher, and A. L. Rheingold, *Inorg. Chem.*, **31**, 473 (1992).

15) O. Poncelet, W. J. Sartain, L. G. Hubert-Pfalzgraf, K. Folting, and K. G. Caulton, *Inorg. Chem.*, **28**, 263 (1989).

16) T. Okano, M. Matsuoka, M. Kinoshita, and J. Kiji, *Nippon Kagaku Kaishi*, in press.